



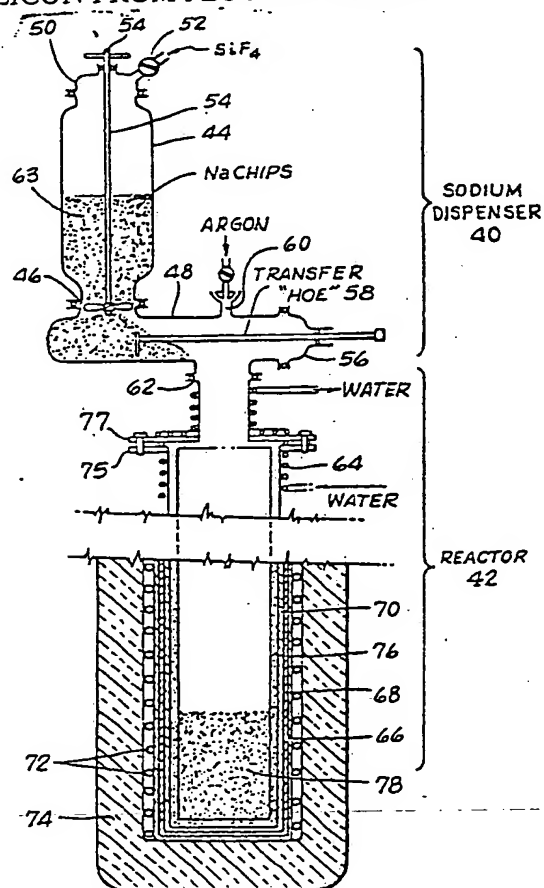
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(54) Title: PROCESS AND APPARATUS FOR OBTAINING SILICON FROM FLUOSILICIC ACID

## (57) Abstract

Process for producing high purity solar grade silicon by reaction (12) of silicon tetrafluoride with sodium which is carried out inside a powder lined reaction container (76) enclosed within a reactor (42). The powder is selected from at least one fluoride or silicate of alkali or alkaline earth metals or an oxide of silicon or a powder of reaction products (78) the powder liner (76) forming the container being capable of withstanding heating below the melting point of sodium fluoride without sintering or melting. The powder liner (76) forming the container is made sufficiently thick to provide a thermal barrier, prevent bonding or adhesion of the reaction products to the support substrate thereby providing easy release of the reaction products (78).



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PROCESS AND APPARATUS FOR OBTAINING SILICON  
FROM FLUOSILICIC ACID

BACKGROUND OF THE INVENTION

ORIGIN OF INVENTION

- 10 The United States Government has rights in this invention pursuant to JPL/DOE Contract No. 954471-NAS 7-100 awarded by the U.S. Department of Energy.

FIELD OF INVENTION

- 15 Silicon is, at present, the most important material in modern semiconductor technology and is finding increased use in solar cells for the photovoltaic generation of electricity. In view of the importance of the solar cell application, the stringent requirements for purity and low cost and further in view of the orientation of the work done, the  
20 process and apparatus is described primarily in the context of production of silicon for solar cell use. However, it is

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to be understood that both the process and apparatus used are generally useful in the production of silicon for whatever end use.

5 A major deterrent to the development of practical solar photovoltaic systems is the cost of high purity silicon. With today's technology, approximately twenty percent of the total cost of a silicon solar cell is ascribed to the silicon material alone. That is, the cost of the silicon material produced by the conventional hydrogen reduction of chlorosilanes constitutes at least twenty percent of the cost of  
10 producing the cell. It is estimated that the cost of the silicon must be reduced by almost an order of magnitude before silicon solar photovoltaic panels will prove to be economically feasible as a power source. The fact that the  
15 chlorosilane processes require multiple separations, are so energy intensive and require such large capital investments indicate that cost of the silicon can not be reduced sufficiently to make silicon solar cells economically feasible without a major process change. As a consequence, an  
20 approach to the production of solar grade silicon which is less complex, less energy intensive and which requires less capital equipment is required.

#### TECHNICAL FIELD OF THE INVENTION

25 It has been found that silicon of more than sufficient purity to meet the solar cell applications can be produced



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within the economic requirements from the metallic reduction of silicon fluoride. Preferably, the silicon fluoride is prepared from an aqueous solution of fluosilicic acid, a low cost waste by-product of the phosphate fertilizer industry by treatment with a metal fluoride which precipitates the corresponding fluosilicate. This salt is filtered, washed, dried and thermally decomposed to produce the corresponding silicon tetrafluoride and metal fluoride which can be recycled to the precipitation step. The silicon tetrafluoride is then reduced by a suitable reducing metal and the products of reactions are treated to extract the silicon. Each of the steps is described in detail using sodium as typical reducing agent, and sodium fluoride as typical precipitating fluoride but the concept applies as well to other reducing metals and metal fluorides that can reduce silicon fluoride and form fluosilicates.

The process in one form is described in detail in an article entitled Silicon by Sodium Reduction of Silicon Tetrafluoride authored by A. Sanjurjo, L. Nanis, K. Sancier, R. Bartlett and V.J. Kapur in the Journal of the Electrochemical Society Vol. 128, No. 1, January 1981 and the subject matter of that article is specifically incorporated herein by reference.

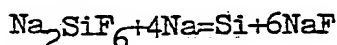
BACKGROUND ART



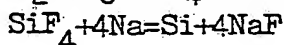
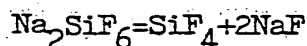
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There are available systems for the production of silicon utilizing some of the reactions of the present system. For example, Joseph Eringer in U.S. Patent 2,172,969 describes a process wherein sodium silico-fluoride is mixed with sodium in powder form and placed in a crucible which is heated and in the upper part of which two pieces of copper wire gauze are placed parallel to each other. The space between the pieces of gauze, which can also be heated, is filled with copper wool. When the crucible has been filled and closed, it is heated to about 500 degrees C. At this temperature, reaction takes place and silicon and sodium fluoride are formed whereby the silicon which is mechanically expelled by the sudden increase in pressure is collected in chambers or towers connected to the furnace.

The equation of the reaction is as follows:



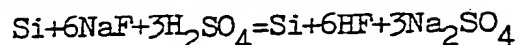
or this can be expressed:



After the reaction product has been cooled at least to 200 degrees C it is finely divided and is treated with water or heat treated with dilute 1:1 sulfuric acid. Hydrogen fluoride gas is liberated (which latter can then be made into hydrofluoric acid or a metallic fluoride) metallic sulphates are produced and the silicon separates out on the surface in amorphous form as shining metallic froth.

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The reaction expressed in equation form is:



After the silicon has been separated from the metallic sulphate solution, it is again washed and is dried at 80  
5 degrees C. The silicon obtained in this way is in the form of an impalpable redish or grey-brown powder which discolors strongly and which, even if the raw products were impure, contains a minimum of 96-97% silicon. The yield amounts to about 87% of the theoretically possible yield.

10 Robert Aries reports in U.S. patent no. 3,041,145 that attempts made to reduce silicon halides by the use of sodium vapor have not led to a commercially successful process. He gives as an example the process discussed in the Eringer patent, supra, and points out 96%-97% purity is entirely  
15 outside the range of purity required for silicon to be used for photocells, semiconductor rectifiers, diodes, and various types of electronic equipment. As has already been discussed, the conventional hydrogen reduction of chlorosilanes especially with the electro-deposition techniques used, is  
20 too energy intensive to be economical.

Aries ascribes the purity problem to impurities in the sodium used in the reduction reaction and teaches that further elaborate and expensive purification of the purest  
25 available commercial grade sodium is required to produce silicon of solar or semiconductor grade.

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It has been determined that silicon of the desired grade is obtained without the elaborate purification of commercial grade sodium provided the proper environment is maintained during the reduction reaction and the product is properly isolated from contaminating atmosphere and container walls until the reaction is complete and solid silicon which is below reaction temperature is formed. It has further been determined that the isolation from container walls should be such that the reaction product does not adhere and can be removed by a simple dumping process.

## SUMMARY AND OBJECTS OF INVENTION

In carrying out the present invention sodium fluosilicate  $\text{Na}_2\text{SiF}_6$  is precipitated from fluosilicic acid followed by thermal decomposition of the fluosilicate to silicon tetrafluoride  $\text{SiF}_4$ . The  $\text{SiF}_4$  is then reduced by an alkali metal, preferably Na, to obtain silicon which is separated from the mix, preferably by leach separation. Purity of reaction products are maintained through isolation from reaction container walls by non-contaminating salts, such as NaF,  $\text{CaF}_2$ ,  $\text{BaF}_2$ ,  $\text{MgF}_2$ , et al, but preferably NaF, so that the reaction products do not adhere to the walls and are easily removed from the container without the use of contaminating tools.

The invention has for its principal object the provision of a process for obtaining silicon of sufficient purity to





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produce solar photovoltaic cells inexpensively enough to make their use practical.

5 A further object of this invention is to provide a process by means of which silicon can be obtained which is substantially free of impurities starting with relatively inexpensive and impure fluosilicic acid.

10 A still further object of this invention is to provide a high purity silicon by isolation of silicon producing reaction products from contaminating reaction chamber walls in such a way that the reaction product does not adhere to the walls and is easily removed.

15 The novel features which are believed to be characteristic of the invention are set forth with particularity in the appended claims. The invention itself, however, both as to its organization and method of operation, together with further objects and advantages thereof may best be understood by reference to the following description taken in connection with the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

20 Figure 1 is a flow diagram illustrating a preferred embodiment of the process for producing high purity silicon by the leach process;



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Figure 2 is a graph illustrating the time, temperature and pressure characteristics of the silicon fluoride and sodium reaction showing time in minutes plotted along the axis of abscissae and temperature in degrees C and pressure (torr) plotted along the axis of ordinates;

Figure 3 is a somewhat diagrammatic central vertical section through a solid sodium dispenser and reactor unit showing reaction products and a reactor liner according to the present invention;

Figures 4 and 5 are central vertical sections through broken away portions of reactors showing other reactor and liner configurations according to the present invention; and

Figure 6 is a diagrammatic central vertical section through a drip feed liquid sodium dispenser and reactor showing a reactor liner suitable for such a unit.

#### DESCRIPTION OF PREFERRED EMBODIMENTS

A preferred embodiment of the process for production of pure silicon starting with inexpensive commercial grade fluosilicic acid is illustrated in the flow diagram of Figure 1.

The overall process consists of three major operations which encompass a series of steps. The first major operation (shown in brackets 10 in the drawing) includes the step of precipitation of sodium fluosilicate from fluosilicic acid



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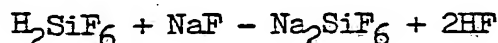
followed by generation of silicon tetrafluoride gas. The second major operation (brackets 12 on the drawing) comprises the reduction of silicon tetrafluoride to silicon, preferably by sodium and the third operation (brackets 14) involves the separation of silicon from the mixture of silicon and sodium fluoride.

Consider first the steps for generation of silicon tetrafluoride (operation 10). The preferred starting source of silicon is an aqueous solution of fluosilicic acid ( $\text{H}_2\text{SiF}_6$ ), a waste product of the phosphate fertilizer industry, that is inexpensive and available in large quantities.

Fluosilicic acid of commercial grade [23 weight percent (w%)] has also been used directly as received without purification or special treatment and is shown as the silicon source 16 in Figure 1. As another alternative, fluosilicic acid is obtained by treating silica, or silicates (natural or artificially made) with hydrogen fluoride. The  $\text{SiF}_6$  ion is then precipitated in sodium fluosilicate  $\text{Na}_2\text{SiF}_6$ , by adding a sodium salt to the solution (step 18). Other salts such as NaF, NaOH, NaCl, or similar salts of the elements in groups IA and IIA of the periodic table are all candidates. The major selection criteria are, low solubility of the corresponding fluosilicate, high solubility of impurities in the supernatant solution, high solubility of the precipitating fluoride salt, and non-hygroscopic character of the fluosilicate.

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Based on these criteria, the preferred fluosilicates in order of preference are  $\text{Na}_2\text{SiF}_6$ ,  $\text{K}_2\text{SiF}_6$  and  $\text{BaSiF}_6$ . Using the preferred NaF as the precipitating salt, the hydrogen of the fluosilicic acid is displaced by the sodium to form sodium fluosilicate, a highly stable, nonhygroscopic, white powder, and sodium fluoride which is recycled. In equation form the reaction is



As an example, Sodium fluosilicate was precipitated by adding solid sodium fluoride directly to the as received commercial grade fluosilicic acid 18. The yield was a supernatant liquid containing mostly HF and some NaF and  $\text{H}_2\text{SiF}_6$  along with the sodium fluosilicate. HF is also given off (20). The supernatant fluid was removed and the sodium fluosilicate washed with cold distilled water to remove any remaining HF and  $\text{H}_2\text{SiF}_6$ . After filtering and drying in an oven at 200 degrees C, a minimum yield of 92% of pure sodium fluosilicate 22 (determined by x-ray diffraction) was obtained. The product sodium fluosilicate is a nonhygroscopic white powder that is very stable at room temperature and thus provides an excellent means for storing the silicon source before it is decomposed to silicon tetrafluoride.

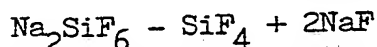
Precipitation under the just described conditions acts as a purification step, with most impurities in the original fluosilicic acid staying in solution. This effect is increased by adding suitable complexing agents to the



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fluosilicic acid solution previous to the precipitation. Both inorganic complexing agents such as ammonia and organic agents such as EDTA (ethylenediaminetetraacetic acid) help to keep transition metal ions in solution during precipitation of the fluosilicate.

The fluosilicate is thermally decomposed 24, thus,



to give the solid sodium fluoride, which is recycled 26, and to generate the  $\text{SiF}_4$  gas 28. The decomposition does not take place appreciably at temperatures below 400 degrees C. Therefore, impurities which are volatile at this temperature can easily be removed by a vacuum treatment below this temperature. The decomposition of Na takes place at temperatures between 500 and 700 degrees C. Impurities left in the solid phase are typically transition metal fluorides such as Fe, Ni, Cu, etc. , whose volatility at temperatures below 700 degrees C is very low and therefore do not contaminate the  $\text{SiF}_4$  gas. The gas thus produced can be fed directly to the reduction reactor or it can be stored for future use.

In separate experiments, it was determined that  $\text{SiF}_4$  gas at a pressure of 0.4 atm is in equilibrium at 650 degrees C with solid  $\text{Na}_2\text{SiF}_6$  and NaF. Therefore, as  $\text{SiF}_4$  is needed, the  $\text{Na}_2\text{SiF}_6$  is thermally decomposed (Fig.1) at 650 degrees C in a graphite-lined, gas-tight stainless steel retort. Gaseous  $\text{SiF}_4$  evolved at 650 degrees C was condensed as a white solid in a storage cylinder (cooled by liquid nitrogen)

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attached to the retort. The  $\text{SiF}_4$  gas was allowed to expand by warming of the storage cylinder to room temperature and was fed into the reactor as needed.  $\text{SiF}_4$  gas prepared in this manner was determined by mass spectrometric analysis to be more pure than commercial grade  $\text{SiF}_4$ , as shown in Table I. Ions formed from the sample gas were identified from the observed mass numbers, isotopic distribution and threshold appearance potentials. The detection limit was better than 0.005%. Positively identified gaseous impurities are listed in Table I; no metallic impurities were detected. Peaks corresponding to B compounds, such as  $\text{BF}_3$ , were specially checked, but none were found.

Although the  $\text{SiF}_4$  produced from  $\text{H}_2\text{SiF}_6$  has less impurity, the commercial grade  $\text{SiF}_4$  was also used for experimental convenience. The possible presence of metallic impurities in commercial  $\text{SiF}_4$  was determined by bubbling the gas through high purity water and treating the resulting slurry with an excess of HF to drive off Si as  $\text{SiF}_4$ . The final clear solution was then analyzed by plasma emission spectroscopy (PES). The results are listed in Table II, together with PES analysis of the waste by product  $\text{H}_2\text{SiF}_6$  and the NaF used to precipitate  $\text{Na}_2\text{SiF}_6$  (18 and 22 Fig. 1). Comparison of the first two columns of Table II with column three shows that the concentration of some elements, e.g., Li, B, V, Mn, Co, K, and Cu, were unchanged by precipitation of  $\text{Na}_2\text{SiF}_6$  whereas the elements Mg, Ca, Al, P, As, and Mo were diminished by a factor of 5-10. Some elements were

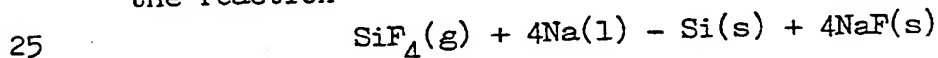
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concentrated into the  $\text{Na}_2\text{SiF}_6$ , namely Cr, Fe, and Ni. The fourth column in Table II is representative of the impurity content to be found in  $\text{SiF}_4$  gas prepared on a commercial scale. The low content of P is of special significance for both semiconductor and solar cell applications. Elements known to reduce solar cell efficiency (V, Cr, Fe, Mo) are uniformly low in commercial grade  $\text{SiF}_4$ . Only Mn, As, and Al are of comparable concentration in both  $\text{Na}_2\text{SiF}_6$  and  $\text{SiF}_4$  at the 1 ppm or less level.

Table I Mass spectrometric analysis of  $\text{SiF}_4$

| Ion                                 | $\text{SiF}_4$ prepared from $\text{H}_2\text{SiF}_6$ (%) | $\text{SiF}_4$ commercial (%) |
|-------------------------------------|---|-------------------------------|
| $\text{SiF}_3^+$                    | 96.9  | 93.6                          |
| $\text{Si}_2\text{OF}_6^+$          | 3.04  | 4.24                          |
| $\text{SiOF}_2^+$                   | (-)   | 1.79                          |
| $\text{CCl}_3^+$                    | (-)   | 0.159                         |
| $\text{SiO}_2\text{F}_2^+$          | 0.076   | 0.098                         |
| $\text{Si}_2\text{O}_2\text{F}_4^+$ | (-)   | 0.081                         |
| $\text{SiO}_2^+$                    | (-)   | 0.035                         |

$\text{SiF}_4/\text{Na}$  reaction, the central operation of the pure Si process, (Fig. 1) is the reduction of  $\text{SiF}_4$  by Na according to the reaction



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Table II. Plasma emission spectroscopy analysis, ppm(wt)

| Element | H <sub>2</sub> SiF <sub>6</sub> | NaF  | Na <sub>2</sub> SiF <sub>6</sub> | SiF <sub>4</sub> |
|---------|---------------------------------|------|----------------------------------|------------------|
| Li      | 0.1                             | (-)  | 0.2                              | 0.01             |
| Na      | 460                             | (-)  | (-)                              | 1.8              |
| K       | 9.0                             | (-)  | 8.0                              | 0.3              |
| Mg      | 55                              | (-)  | 6.4                              | 2.3              |
| Ca      | 110                             | 10   | 18                               | 1.6              |
| B       | 1.0                             | (-)  | 0.8                              | <0.01            |
| Al      | 8.0                             | <2.5 | 1.3                              | 1.2              |
| P       | 33                              | (-)  | 5                                | 0.08             |
| As      | 8.8                             | (-)  | 0.2                              | 0.28             |
| V       | 0.3                             | <5   | 0.3                              | <0.01            |
| Cr      | 0.8                             | <3.5 | 8.8                              | <0.01            |
| Mn      | 0.2                             | <4   | 0.4                              | 0.16             |
| Fe      | 13                              | <7   | 38                               | 0.04             |
| Co      | 0.54                            | (-)  | 0.7                              | <0.01            |
| Ni      | 1.17                            | <8   | 4.2                              | <0.01            |
| Cu      | 0.12                            | <4   | 0.6                              | <0.01            |
| Zn      | 1.4                             | (-)  | 1                                | <0.01            |
| Pb      | 14.5                            | (-)  | 5                                | 0.03             |
| Mo      | 11                              | (-)  | 1.0                              | <0.01            |

Although this reaction is thermodynamically favored at room temperature, it has been found experimentally that Na has to be heated to about 150 degrees C before any appreciable reaction can be observed. Once the reaction has been



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initiated the released heat raises the temperature of the reactant (Na) which in turn increases the reaction rate. Under adiabatic conditions, a temperature of 2200 K is predicted for the reaction with the stoichiometric quantities of  $\text{SiF}_4$  and Na. In practical reactors, rapid consumption of gaseous  $\text{SiF}_4$  produces a pressure decrease. The kinetic behavior of the Na- $\text{SiF}_4$  reaction is complex because of the interplay of several factors, e.g., pressure of  $\text{SiF}_4$ , vaporization of Na, local temperature, porosity of two solid products, and transport of  $\text{SiF}_4$  and Na vapor through the product crust that forms on the liquid Na.

Although only preliminary studies have been made of the kinetics, the general features of this reaction have been surveyed. In a series of experiments to estimate reaction temperature 5 grams of Na were loaded in a Ni crucible (3 cm ID, 4 cm high) and heated in  $\text{SiF}_4$  initially at 1 atm pressure. The Na surface tarnished at around 130 degrees C, with the formation of a thin brown film. As the temperature increased, the color of the surface film gradually changed from light brown to brown and finally to almost black. The

$\text{SiF}_4$  Na reaction became rapid at 160 degrees +/- 10 degrees C and liberated a large amount of heat, as indicated by a sudden rise in reaction temperature. As shown in Fig. 2, the pressure in the reactor typically decreased slightly until the temperature increased sharply, with an associated rapid decrease in  $\text{SiF}_4$  pressure. The reaction lasts for several seconds only. For  $\text{SiF}_4$  pressures below 0.3 atm the

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reaction mass was observed to glow at a dull red heat. For higher pressure, a characteristic flame was observed. The shortest reaction time (20 sec) and the highest temperatures (about 1400 degrees C) were obtained when the initial pressure of  $\text{SiF}_4$  was around 1 atm. In addition, complete consumption of Na was obtained for 1 atm  $\text{SiF}_4$ . When scale-up of this reaction was attempted by loading larger amounts of Na, it was found that as the depth of the Na pool increased, the amount of Na remaining unreacted also increased. The product formed a crust on top of the Na surface, building a diffusion barrier for the reactants. As the barrier thickness increased, the reaction slowed and eventually stopped.

For separation (operation 14 Fig. 1) of the silicon from the products of reduction, the silicon and sodium are removed (step 30) and combined with water (32) and a selected acid. The resultant silicon (34) and sodium fluoride (36) are then separated. The leaching and separation process is described in detail below in connection with the scaled up system.

On the basis of studies of the parameters that affect the reaction, a system was developed that is capable of producing Si at the rate of 0.5 kg/hr in a batch mode. The reactor system is shown somewhat schematically in Fig. 3. The upper section 40 of the system illustrated constitutes a sodium dispenser and the lower section 42 is the reactor section where the reaction takes place between the Na and the  $\text{SiF}_4$ . In the illustrated embodiment, the sodium



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dispenser section 40 is a Pyrex glass vessel or hopper which is coated internally with epoxy resin on all glass surfaces that may contact Na. The sodium dispensing section 40 has a vertical cylindrical entry section 44 for receiving and  
5 holding the Na used in the process. The entry section 44 has its lower end open to, and sealed 46 to, one end (left in the drawing) of a horizontal cylindrical reactor feeding section 48. In order to receive the Na, the upper end of the entry or storage section 44 is provided with a removably  
10 sealed end bell 50 which has a closable entry port 52 to receive  $\text{Si}_4$  for the reaction and an agitator rod 54 which extends into the Na receiving entry chamber 44 for agitating its contents and forcing Na into the lower reactor feeding section 48. The reactor feeding section 48 is permanently  
15 sealed at the end adjacent the port 46 from the entry section 44 and has a sealing end bell 56 which accommodates a horizontal rod-like Na transferring "hoe" mechanism 58 or screw feeder (not shown). The upper wall has a closable entry port 60 to allow gas flow and the lower wall is open  
20 to a reactor communicating cylindrical port section 62.

Sodium chips 63 were prepared by feeding 225g blocks of sodium (6 cm diameter rod, cut longitudinally) into a modified food processor with rotating cutting blades. The chips were fed into the entry section 44 of the Na dispenser 40  
25 using a blanket of argon to minimize contact with atmospheric oxygen and moisture. While Na chips 63 were being introduced into the top of the storage chamber 44 of the

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dispenser 40 (2kg capacity), dry argon was introduced into the reactor feeding section 48 and flowed up through the chamber 44. The Na chips 63 were transferred from the storage chamber 44 to the reactor 42 by means of a horizontal "hoe" mechanism 58 or screw feeder (not shown). Downward flow of Na chips 63 in the storage chamber 44 was aided by agitation of the vertical rod 54. Notice that the throat-like cylindrical port section 62 of the Na dispenser 40 is surrounded by water cooling coils 64 effectively to keep the temperature in the sodium dispenser 40 so low that reaction does not take place between the Na and  $\text{SiF}_4$  until they are in the reactor.

The reduction reaction (Fig. 1 operation 12) takes place in the lower reactor section 42 of the reactor system. As illustrated, the reaction chamber or vessel 66 of the reactor system is made of stainless steel or Inconel (20 cm diameter and 90 cm high) and is fitted with a sheet nickel liner 68 (18 cm diameter and 60 cm high) and an inner liner of sheet Grafoil 70 (18 cm diameter and 90 cm high). In order to heat the reactor and thus assure that the reaction takes place, the outside of the reactor chamber or vessel 66 is wrapped with four sets of heavy duty electrical heating tapes 72 (rated for use to 800 degrees C). For heating efficiency and to reduce heat radiation from the reactor, the heating coils 72 are covered with Kaowool insulation 74 (1.3 cm thick). The top of the reactor 42 and the bottom of the cylindrical port section 62 of the Na dispenser 40 both

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- have flanges (75 and 77 respectively) that are connected together. Note that the water cooled tubing 64 extends around the entire flanged section to prevent the reaction from moving up into the Na dispensing section 40. In this connection, it has been found experimentally that Na reacts with  $\text{SiF}_4$  only above 150 degrees C. Therefore, as long as the cooling coils 64 maintain the Na feed area below this temperature, premature reaction at the feed port is prevented.
- As previously pointed out, when the Na reduction of  $\text{SiF}_4$  takes place under adiabatic conditions, a temperature of 2200 K is predicted for reaction of stoichiometric quantities. Thus, any impurities in reactor wall materials will be picked up in the reaction product. Further, at such high temperatures, the reaction products adhere tightly to reactor walls. This is particularly true for walls of Ni and in fact, where Ni liners are used, they melt into the reaction product. In either case, separation of the reaction product from the wall material introduces another source of impurities. It has been found that the use of certain liners, particularly powder liners or liners made from powder slurries which slough off rather than adhere to the reactor wall avoids these problems by eliminating or markedly reducing impurity pick-up from the reactor walls, allowing easy removal of the reaction products by eliminating their adherence to reactor walls and liners, and for some preferred liner coatings, seeding is aided. Such an inner coating powder

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liner 76 is used on the inner wall of the reactors 42 illustrated. The powder liner 76 in each case lines the inner walls of the reactor 42 in such a manner as effectively to constitute a powder reaction container in which the reaction takes place. A preferred coating is NaF which has all of the favorable properties. When the reaction temperature is higher than the melting point of NaF (988 degrees C), a clean phase segregation occurs, thus facilitating the extraction of Si. However, many other materials are candidates. For example, metal fluorides such as  $\text{CaF}_2$ ,  $\text{BaF}_2$ ,  $\text{MgF}_2$ , et al. SiC, graphite and other noncontaminating ceramics are also candidates. In fact, any material selected from a powder of at least one fluoride or silicate of alkali or alkaline earth metals or an oxide of silicon or a powder reaction products of this reaction will perform the function.

In operating the reactor 42 (after loading the Na chips 63 in the presence of Argon, as described above), the system was evacuated, then filled with  $\text{SiF}_4$  gas to a pressure of about 1 atm. Reaction was initiated as soon as Na chips were dropped to the bottom of the reactor, which was preheated to 400 degrees C. Reaction was sustained by manually adding Na chips 63 at a rate sufficient to maintain a given  $\text{SiF}_4$  flow rate, as indicated by an electronic flowmeter (not shown). The maximum flow rate used was 380 liters  $\text{SiF}_4$ /hr and a production rate of 0.5 kg Si/hr. During the operation of the reactor 42, the temperature of the reactor

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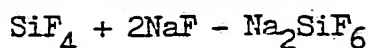
walls in the region of the reaction products 78 rose to 600 degrees - 650 degrees C, as indicated by external thermocouples (not shown). Without a powder liner 76, the temperature of the nickel liner reached the melting temperature of NaF (998 degrees C), indicated by molten NaF observed on the outside of the nickel liner near seams as the reaction zone progressed upward.

After each  $\text{SiF}_4$ -Na run was completed, the reaction products 78 completely occupied the cylindrical space inside the Ni-Grafoil liner 68-70. Without the powder liner 76, the reaction products 78 are difficult to separate, however, they were pulverized with plastic equipment and routine checks were made for the presence of unreacted Na by acid titration. An important parameter regulating the rate and extent of the reaction is the surface-to-volume ratio of the Na feed. For the 18 cm diam Inconel reactor, no unreacted Na was observed in the reaction products even for the highest Na addition rate used (1.4 kg/hr) when the Na chips had a surface to volume ratio of about  $20 \text{ cm}^{-1}$ .

The relative amounts of Si, NaF, and  $\text{Na}_2\text{SiF}_6$  were determined by x-ray diffraction using standard mixtures. The weight fraction of  $\text{Na}_2\text{SiF}_6$  was determined from the ratio of the peak intensities of  $\text{Na}_2\text{SiF}_6$  and KCl reference additive. The method is rapid and accurate to about  $\pm 5\%$ . The presence of  $\text{Na}_2\text{SiF}_6$  was also cross-checked by thermogravimetry. The presence of  $\text{Na}_2\text{SiF}_6$  in the reaction product mixture is an

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indication of possible side reaction according to



which is the reverse of the decomposition reaction used for  $\text{SiF}_4$  generation in step 18 (Fig. 1) of the overall process.

5 When the reactor walls are kept above 600 degrees C, the formation of by-product  $\text{Na}_2\text{SiF}_6$  was less than 2 w%.

Figures 4, 5 and 6 show alternate structures for the reactor 42 of the system. The reactor structures all have common elements which, for simplicity of description and drawings, are given the same reference numerals in all Figures. That is, the reactor 42 of Figure 4 has all of the same elements as that of Figure 3 except it does not utilize a Grafoil liner (70 Fig. 3) between the powder liner 76 and the Ni (Inconel) lining 68. In fact, the use of the powder liner 76 simplifies the reactor construction considerably and the reactor 42 of Figure 5 is further simplified in that it utilizes the powder liner 76 adjacent the single walled reactor container 66 which is preferably of stainless steel but may be of materials such as Ni or high temperature glass.

The reactor 42 used with the liquid Na feed system of Figure 6 has the same elements as that of Figure 5 in that it has the outer cover of insulation 74, heater coils 72 between stainless steel reactor vessel 66 (inside) and the outer insulation, a Ni liner 68 lining the reactor container 66



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and a powder liner 76 at the bottom and part way up the inner wall. The reason that it is only necessary to use the powder liner 76 near the bottom in the liquid feed system shown is that initially the reaction takes place only at the bottom of the reactor vessel 66 and the reaction product 78 builds up in a "stalagmitic" manner so that it does not touch the reactor vessel walls except in a limited area at the container bottom.

Note also that the heater coils 72 surround only a limited part of the bottom of the reactor vessel. This is for the reason that once the reduction reaction starts at the bottom, the exothermic reaction supplies sufficient heat to keep the reaction going as the reaction product 78 builds up from the bottom.

As described above, the system of Figure 6 is a liquid Na feed. The liquid Na feed head includes an end bell 80 that has a flange 77 secured and sealed to the upper flange 75 on the stainless steel reactor body 66 just as the solid Na delivery head of Figure 3. A valved Na feed tube 84 is centrally (and vertically) positioned in the top of the end bell 80 to introduce individual droplets 86 of Na which can drop directly into the reactor section 42. A valved  $\text{SiF}_4$  feed tube 82 is positioned to deliver  $\text{SiF}_4$  into the top of the end bell 80 so that it flows down around the Na droplets 86 into the reaction chamber. Although not shown, provision is made to keep the Na feed head cool since the Na should be

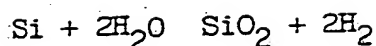
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injected at temperatures below 150 degrees C so that it will not react with the  $\text{SiF}_4$  until it reaches the heated bottom of the reactor chamber 66 as previously described.

5 The final operation 14 in the flow diagram of Figure 1 is the separation of Si from the reaction products 78. Using the powder lined reactors 42 illustrated and described here, it is only necessary to disconnect the reactor section and dump the reaction product 78. Thus, no impurities are introduced from reactor walls or by reason of having to use  
10 contaminating tools to extract the reaction product 78.

The reaction product obtained by the  $\text{SiF}_4$ -Na reaction is a porous, brown mass. This intimate mixture of NaF and Si is readily separated by aqueous leaching. The Si product  
15 obtained after leaching is a brown crystalline powder with particle sizes ranging from submicrometers up to 150  $\mu\text{m}$ . Leaching is performed using 1.0N HCl in a polypropylene container although other acids such as  $\text{H}_2\text{SO}_4$ ,  $\text{CH}_3\text{COOH}$ , and HF are equally effective. The acid normality can vary in the range 0.1 - 1.0N without affecting the leaching process,  
20 which may be monitored by measuring the  $\text{F}^-$  and  $\text{Na}^+$  concentrations in the leachant using ion selective electrodes. When the  $\text{F}^-$  concentration is about  $10^{-5}$  mole/liter, leaching is stopped. The acidification of the leach solution is a precautionary measure to prevent increase in local pH due to  
25 reaction of  $\text{H}_2\text{O}$  with Na, which could, in turn, result in Si loss by oxidation according to the reaction.

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It has been determined experimentally that during leaching in 1.0 N acid, Si can be oxidized at an initial rate of 15 weight percent per hour. The rate of oxidation increases with increased F<sup>-</sup> ion concentration in solutions with pH in the range of -0.8 to 10. The contact time may be minimized by using forced filtration, which yields a 98% complete recovery of Si. Differences in leaching rate due to particle size of the products, temperature of the leaching bath, and amount of stirring were found to be important only during the first minute of leaching.

Several analytical methods have been used to characterize the very low levels of impurity elements in the silicon leached from the products of SiF<sub>4</sub>-Na reaction even when the inner powder container 76 was not employed. Generally, each of the methods is used at the limit of resolution for several elements. For comparison, a reference sample of high purity Si was analyzed in a similar manner to provide a check of spurious readings caused by sample preparation, background effects, and instrumental limitations. The reference material was commercial polycrystalline semiconductor grade Si with resistivity greater than  $1 \times 10^5$  cm.

In Table III, the uncertainty in the methods of emission spectroscopy and spark source mass spectrometry has been taken into account by selecting representative average

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concentrations based on several analyses. A range is indicated for (Fe, Cr, and Cu) where wide variations occur because of its importance, phosphorous was also determined by a wet chemical colorimetric method.

- 5 The process sequence shown in Fig.1 was selected because of the inherent simplicity of the steps and their independent and combined suitability for scale-up. Some purification occurs during precipitation (operation 1, Fig.1) for Mg, Ca, Al, P, and As due to the high solubility of their fluosilicates and fluosalts. Some concentration takes place for Cr, Fe, and Ni, and this effect may be due to coprecipitation of these elements as fluorides since their fluosilicates are very soluble. From Table II, it is clear that most of the purification is accomplished as a result of the thermal decomposition in step 24 (Fig.1). Most transition metal fluorides are in very stable condensed phases at the decomposition temperature (650 degrees C) in step 24 (Fig. 1) and, therefore, will stay in the solid. In addition, volatile fluorides formed during the decomposition of fluosalts such as  $\text{Na}_2\text{TiF}_6$  and  $\text{Na}_2\text{ZrF}_6$  will condense upon cooling of the  $\text{SiF}_4$  gas stream from step 24. The condensed material is then removed from the gas mainstream by in-line fume particle filtration. The presence of any metallic or dopant impurities was not detected using mass spectrometry (Table I) in either the gas produced in the above reaction or in the commercial  $\text{SiF}_4$  gas. The analysis done on the  $\text{SiF}_4$  by passing the gas through high purity water was based on the
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5 hypothesis that impurities should be hydrolyzed and/or trapped in the  $\text{SiO}_2$  formed. The results listed in Table II show that the level of metal impurities in the resulting  $\text{SiO}_2$  is so low that, for practical purposes, the  $\text{SiF}_4$  can be considered free of metallic impurities.

The Na feed, reactor materials, and possible contamination of the product during handling remain as possible sources of impurities in the Si.

10 The impurities in Na can be divided roughly into three types according to their tendency to react with  $\text{SiF}_4$ , as classified by the free energy of reaction. The first type of impurity includes aluminum and elements from the groups IA, IIA and IIIB. The free energy of reaction of  $\text{SiF}_4$  with these impurities ranges from -100 to -200 kcal/mole  $\text{SiF}_4$  at  
15 room temperature and from -50 to -100 kcal/mole  $\text{SiF}_4$  at 1500 K. It is expected, therefore, that even when these impurities are present at the ppm level, they will react with the  $\text{SiF}_4$  to form corresponding fluorides. Subsequently, the fluorides will be dissolved preferentially in the NaF phase.  
20 The second type impurity includes transition metals such as Mo, W, Fe, Co, Ni, and Cu, and the elements P, As, and Sb. These elements exhibit positive free energies of reaction in excess of 100 kcal/mole  $\text{SiF}_4$  and are not expected to react with  $\text{SiF}_4$ . However, it is an experimental fact that the  
25 silicon resulting from the  $\text{SiF}_4$ -Na reaction contains amounts of Fe, Ni, and Cr in proportion to the concentration of

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these elements in the Na feed. The mechanism by which these metals are transferred to the silicon has not yet been studied. In any case, the concentration of Fe, Cr, Ni, and also Ti can be decreased by a factor of about  $10^4$ - $10^6$  for single-pass directional solidification or the Czochralski crystal-pulling procedures used presently for solar cell manufacture. At the resulting levels, these elements would not be detrimental to solar cell performance. Boron represents a third type of impurity. The free energy of reaction of this element with  $\text{SiF}_4$  is positive but small (5-20 kcal/mole  $\text{SiF}_4$  for temperatures up to 1500 K); therefore, some partial reaction can be expected and B will be distributed between the NaF and Si phases. It is noted that the levels of the dopant elements B, P, and As in the reaction Si are the same as in the semiconductor grade silicon used as reference or control. Since it is convenient to have dopant levels as low as possible to permit flexibility in subsequent doping procedures for semiconductor and solar cell applications, the low B and P content (Table III) of Si produced in this process is of advantage. For the results shown in the Tables, contamination from reactor materials was reduced by the use of Ni and Grafoil liners 68 and 70, respectively, (Fig.3) that completely contained the reaction products 78 and avoided contact or direct impurity transfer with the reactor vessel walls 66. The Ni liner served primarily as a mechanical retainer for the Grafoil sheet 70 and did not contact the solid mixed reaction product 78. Both



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Ni and Inconel are selected for use in the reactor 42 (Fig. 3) because of their stability in the presence of fluoride compounds.

5 Contamination during handling the reaction product 76 was a most important source of impurity pick up. Airborne dust could have contacted the products either during the removal from the reactor or during sampling and the physical separation of the reaction product 78 from the reactor vessel 66 required the use of hard contaminating tools. The sodium  
10 feed also requires careful attention as a possible source of impurity pick up and although electronic grade acid and deionized water were used for leaching the NaF, the large volume of liquid used could have contributed to the accumulation of impurity in the silicon. It is noted that the  
15 purity of the silicon produced by the  $\text{SiF}_4$ -Na reaction, even without the protective powder container 76, is at least nominally appropriate for solar cell manufacture. The use of the powder liner or container 76 to eliminate transfer of  
20 impurities from reactor walls and avoid much the impurity contributing handling assures that a high purity solar grade silicon is obtained and it is expected that semiconductor grade silicon is achievable. This is particularly true if pure sodium is used and care is taken at every step to avoid contamination.

25 From the foregoing discussion, it will be understood that the objects of the invention have been carried out and that

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it has been shown experimentally that high purity Si can be prepared as a powder using the inexpensive starting materials  $H_2SiF_6$  and Na. Favorable thermodynamics of the reduction step, easily controlled kinetics, and abundant availability of inexpensive starting materials make this method attractive. Of special interest for semiconductor applications are the low concentrations of B and P impurities in the product Si. The Si produced by the  $SiF_4$ -Na reaction, particularly when produced in the non-contaminating self freeing powder container or liner 76 and if purified further by directional solidification, should be a low cost material suitable for the manufacture of solar cells and other semiconductor products.

While particular embodiments of the invention have been shown, it will, of course be understood that the invention is not limited thereto since many modifications in both process and apparatus employed may be made. It is contemplated that the appended claims will cover any such modifications as fall within the true spirit and scope of the invention.





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## WHAT IS CLAIMED IS:

1. A process for producing low cost, high purity, solar grade silicon by reaction of gaseous silicon tetrafluoride with sodium in substantially stoichiometric quantities to produce a reaction product from which silicon is recovered and wherein said fluoride gas used in the reaction is obtained by thermal decomposition of sodium fluosilicate which is precipitated from aqueous fluosilicic acid generated from phosphate rock conversion to fertilizer, said process comprising:
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- a) carrying out said reaction inside a powder container which is formed from a powder selected from the group consisting of fluorides of alkali and alkaline earth metals, oxides of silicon, powders of reaction products of said reaction, and mixtures thereof;
- 15
- b) allowing said reaction product to cool sufficiently and then gravitationally discharging said reaction product from said powder container for silicon separation.
2. A process for producing low cost, high purity, solar grade silicon by reaction of gaseous silicon tetrafluoride
- 20

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with sodium which comprises:

- 5 a) forming a stable powder liner in a reactor vessel from a powder selected from the group consisting of flourides of alkali and alkaline earth metals, silicates of alkali and alkaline earth metals, oxides of silicon, powders of reaction products of said reaction, and mixtures thereof;
- b) carrying out said reaction within said powder lined vessel with silicon tetrafluoride and sodium residing in said vessel in substantially stoichiometric quantities;
- 10 c) maintaining temperature and silicon tetrafluoride pressure conditions sufficient to allow said reaction to go to substantial completion in said vessel in the absence of external application of heat at or above the melting temperature of sodium fluoride; and
- 15 d) allowing said reaction product to cool sufficiently and the gravitationally discharging said reaction product from said powder lined vessel into a leaching bath.

3. A process for producing high purity silicon by reaction of gaseous silicon tetrafluoride with sodium; wherein sodium



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is charged into a reactor vessel in the form of selected size solids or as selected size liquid drops at temperatures below 150 degrees C, said process comprising:

- 5 a) forming a stable powder container from a powder selected from the group consisting of fluorides of alkali and alkaline earth metals, oxides of silicon, powders of reaction products of the said reaction, and mixtures thereof;
- 10 b) enclosing said powder container within the said reactor vessel;
- c) supplying silicon tetrafluoride at selected positive pressure within said reactor vessel containing said powder container;
- 15 d) heating said reactor vessel at sufficiently elevated temperature to maintain said powder container at a selected temperature below the melting temperature of sodium fluoride;
- 20 e) carrying out said reaction by charging said powder container with a selected amount of sodium sufficient to cause said sodium to react with silicon tetrafluoride residing in said powder container to go to substantial completion under said selected temperature and pressure conditions;
- f) continuing charging said powder container with

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sodium to form sequentially new beds of reaction products at a sodium charging rate sufficient to build up a reaction product column having desirably low amounts of unreacted sodium; and

- 5           g) allowing said reaction product column to cool sufficiently and then gravitationally discharging said product column from said powder container into a leach bath.

4. A process of claim 1, 2 or 3 wherein said powder container wall is formed sufficiently thick to provide a thermal barrier against melting and metallurgical bonding of  
10           said reactor vessel and lining surfaces to said reaction products at high reaction temperatures so that the maximum temperature reached on the outside surfaces of the said powder container during said reaction is less than about the  
15           melting temperature of sodium fluoride.



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5. A process of claim 1, 2 or 3 wherein said powder container is formed from salts selected from the group consisting of NaF, BaF<sub>2</sub>, CaF<sub>2</sub>, MgF<sub>2</sub>, and mixtures thereof.

5 6. A process of claim 1, 2 or 3 wherein said powder container is formed from SiO<sub>2</sub>.

7. A process of claim 1, 2 or 3 wherein said powder container is formed from soluble sodium silicates.

8. A process of claim 1, 2 or 3 wherein said container is formed from silicon.



## AMENDED CLAIMS

(received by the International Bureau on 09 June 1983 (09.06.83))

## WHAT IS CLAIMED IS:

(amended) 1. A process for producing low cost, high purity, solar grade silicon by reaction of gaseous silicon tetrafluoride with sodium in substantially stoichiometric quantities to  
5 produce a reaction product from which silicon is recovered and wherein said fluoride gas used in the reaction is obtained by thermal decomposition of sodium fluosilicate which is precipitated from aqueous fluosilicic acid generated from phosphate rock conversion to fertilizer, said  
10 process is characterized by:

a) carrying out said reaction inside a powder container which is formed from a powder selected from the group consisting of fluorides of alkali and alkaline earth metals, oxides of silicon, powders of reaction products of  
15 said reaction, and mixtures thereof;

b) allowing said reaction product to cool sufficiently and then gravitationally discharging said reaction product from said powder container for silicon separation.

(amended) 2. A process for producing low cost, high purity, solar  
20 grade silicon by reaction of gaseous silicon tetrafluoride

with sodium which is characterized by:

a) forming a stable powder liner in a reactor vessel from a powder selected from the group consisting of flourides of alkali and alkaline earth metals, silicates of  
5 alkali and alkaline earth metals, oxides of silicon, powders of reaction products of said reaction, and mixtures thereof;

b) carrying out said reaction within said powder lined vessel with silicon tetrafluoride and sodium residing in said vessel in substantially stoichiometric quantities;

10 c) maintaining temperature and silicon tetrafluoride pressure conditions sufficient to allow said reaction to go to substantial completion in said vessel in the absence of external application of heat at or above the melting temperature of sodium fluoride; and

15 d) allowing said reaction product to cool sufficiently and gravitationally discharging said reaction product from said powder lined vessel into a leaching bath.

(amended) 3. A process for producing high purity silicon by reaction of gaseous silicon tetrafluoride with sodium; wherein sodium

is charged into a reactor vessel in the form of selected size solids or as selected size liquid drops at temperatures below 150 degrees C, said process is characterized by:

- 5 a) forming a stable powder container from a powder selected from the group consisting of fluorides of alkali and alkaline earth metals, oxides of silicon, powders of reaction products of the said reaction, and mixtures thereof;
- 10 b) enclosing said powder container within the said reactor vessel;
- c) supplying silicon tetrafluoride at selected positive pressure within said reactor vessel containing said powder container;
- 15 d) heating said reactor vessel at sufficiently elevated temperature to maintain said powder container at a selected temperature below the melting temperature of sodium fluoride;
- e) carrying out said reaction by charging said powder container with a selected amount of sodium sufficient to  
20 cause said sodium to react with silicon tetrafluoride residing in said powder container to go to substantial completion under said selected temperature and pressure conditions;
- f) continuing charging said powder container with



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sodium to form sequentially new beds of reaction products at a sodium charging rate sufficient to build up a reaction product column having desirably low amounts of unreacted sodium; and

- 5           g) allowing said reaction product column to cool sufficiently and then gravitationally discharging said product column from said powder container into a leach bath.

4. A process of claim 1, 2 or 3 wherein said powder container wall is formed sufficiently thick to provide a thermal barrier against melting and metallurgical bonding of  
10           said reactor vessel and lining surfaces to said reaction products at high reaction temperatures so that the maximum temperature reached on the outside surfaces of the said powder container during said reaction is less than about the  
15           melting temperature of sodium fluoride.



5. A process of claim 1, 2 or 3 wherein said powder container is formed from salts selected from the group consisting of NaF, BaF<sub>2</sub>, CaF<sub>2</sub>, MgF<sub>2</sub>, and mixtures thereof.
6. A process of claim 1, 2 or 3 wherein said powder container is formed from SiO<sub>2</sub>.
7. A process of claim 1, 2 or 3 wherein said powder container is formed from soluble sodium silicates.
- (amended) 8. A process of claim 1, 2 or 3 wherein said container is formed from powder silicon.

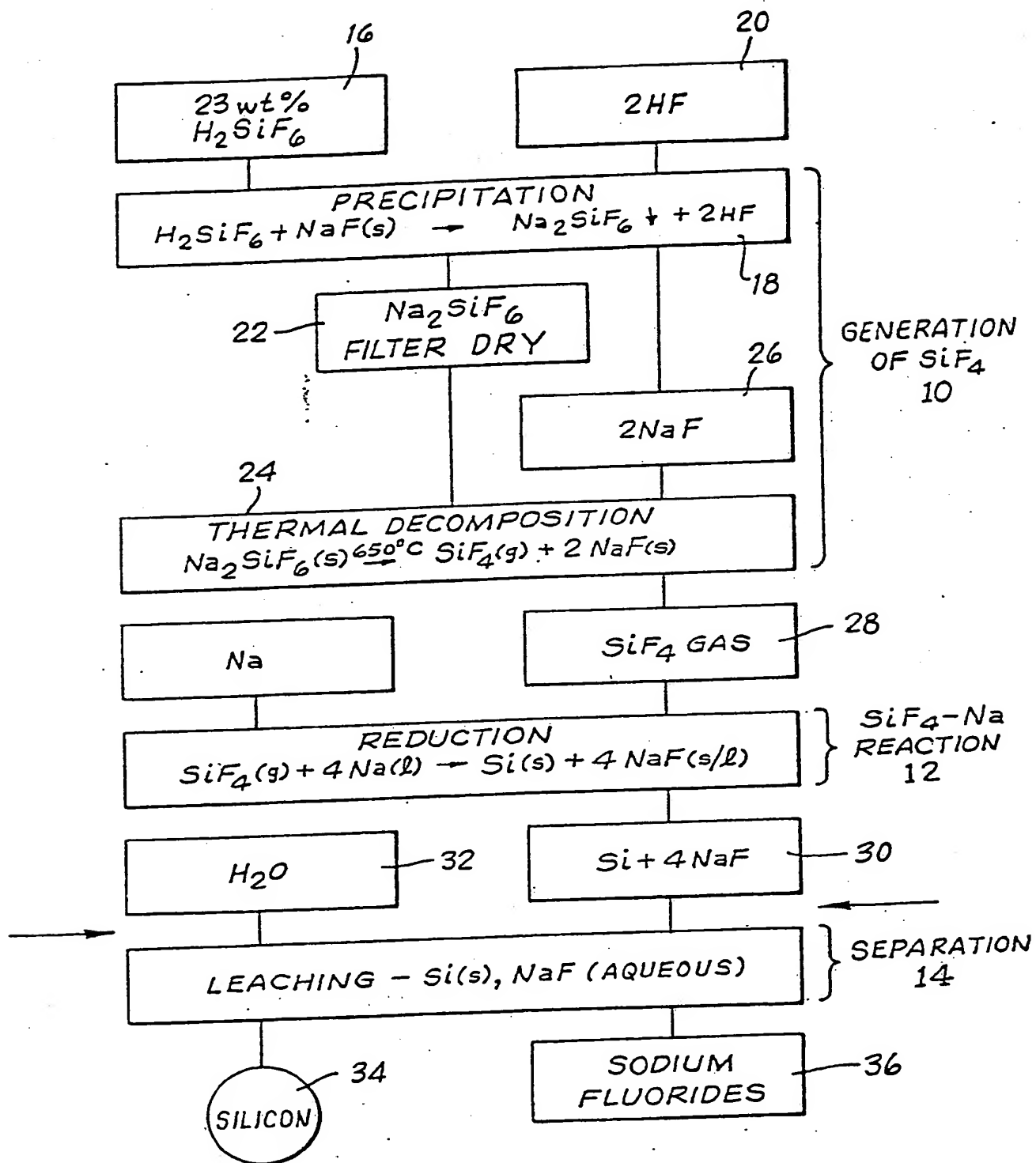


FIG. 1



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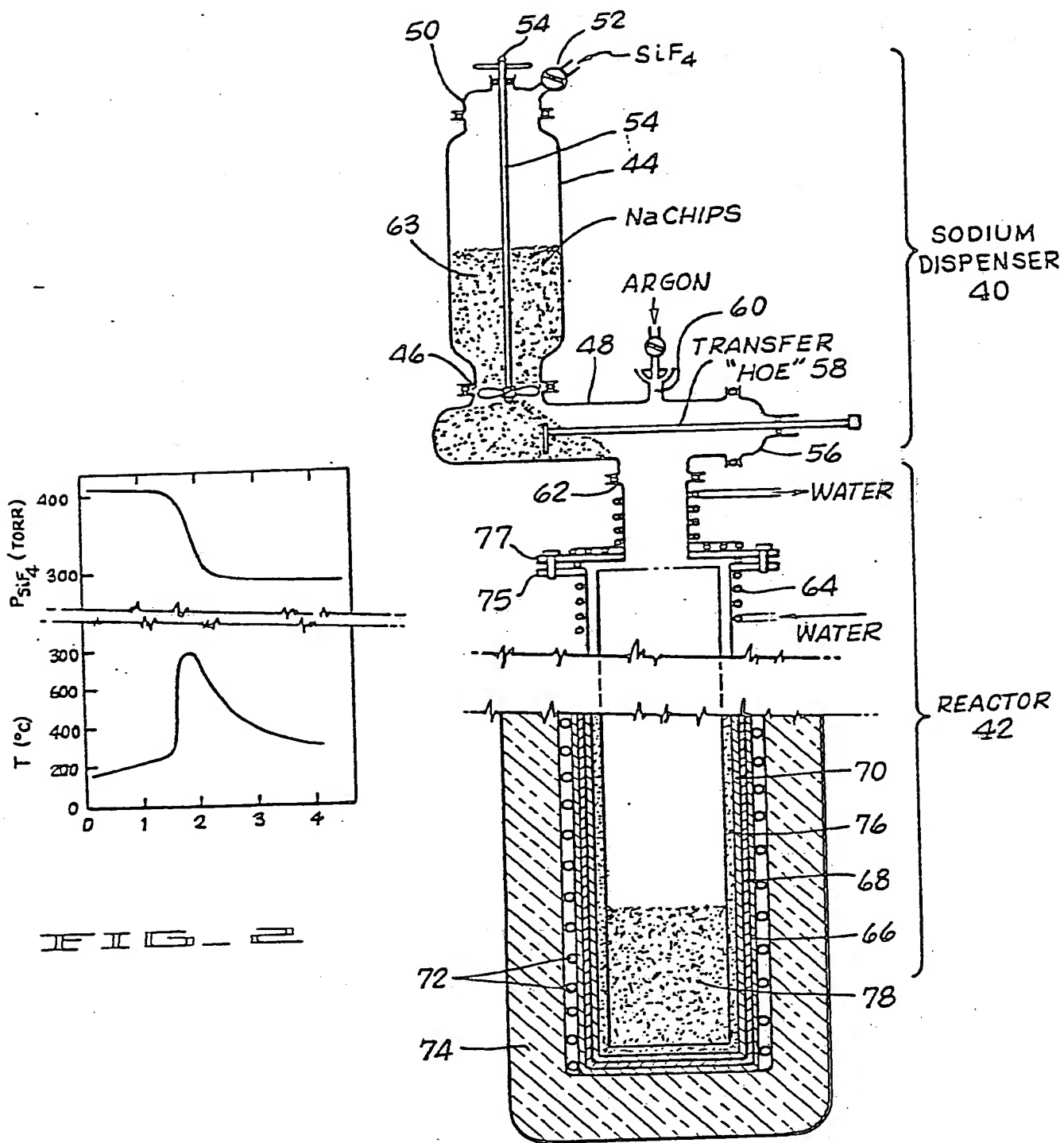


FIG. 2

FIG. 3



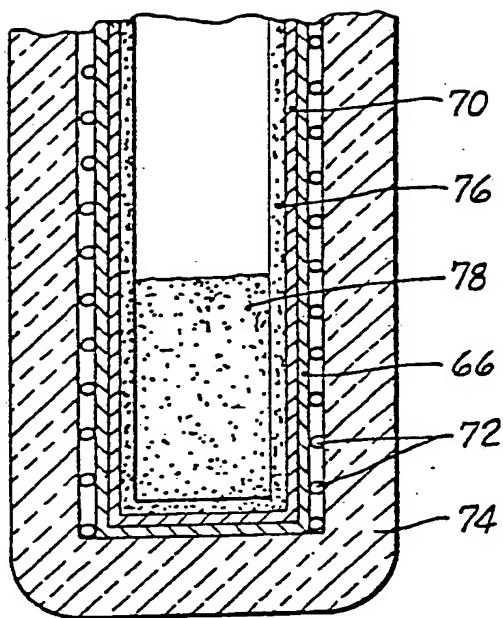


FIG. 4

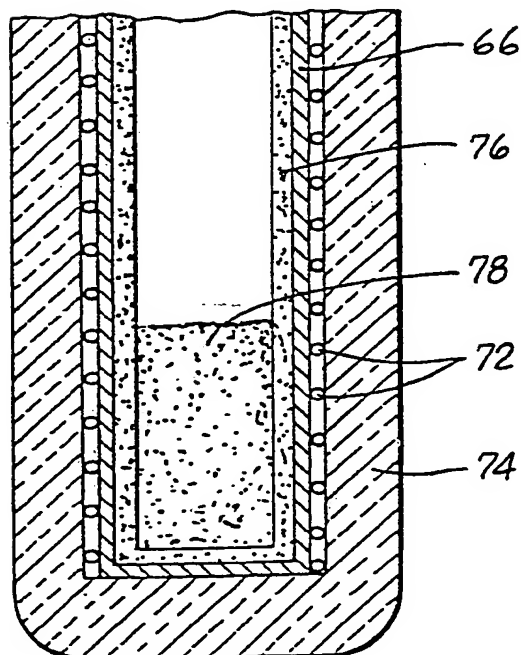


FIG. 5

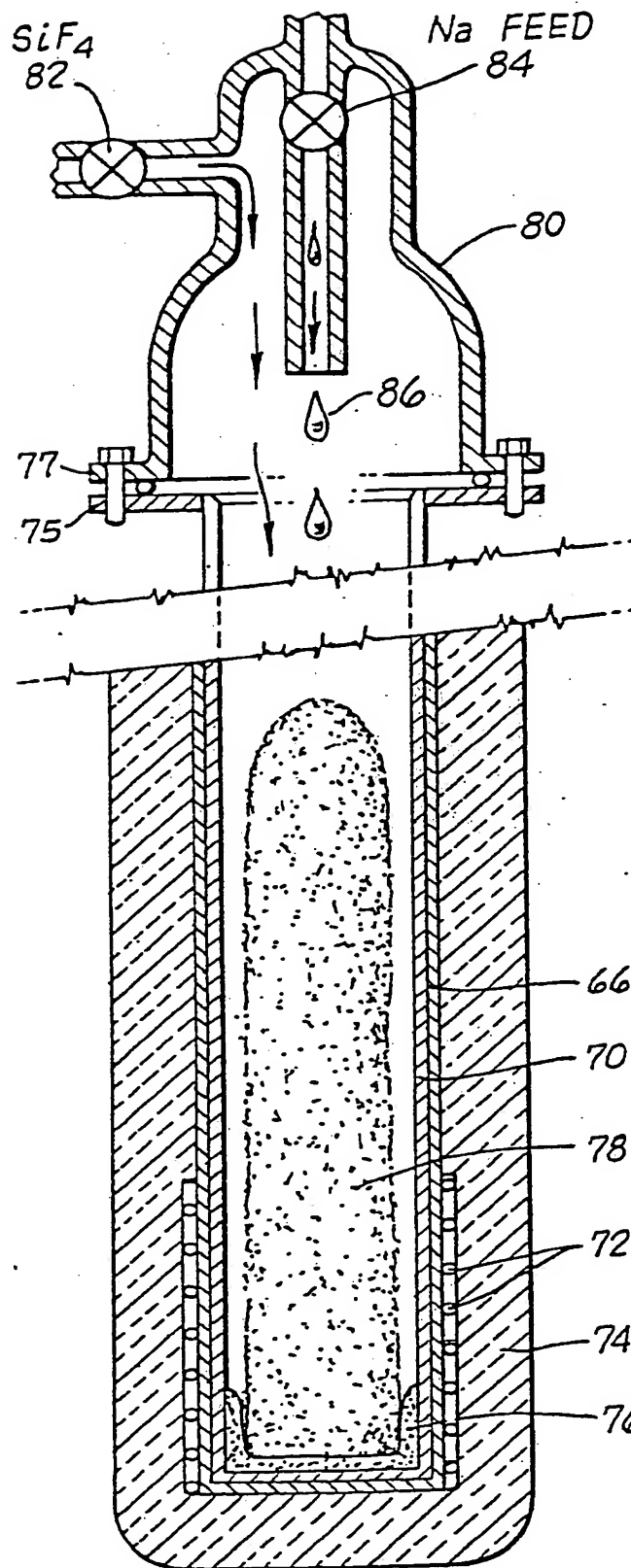


FIG. 6

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US82/01795

| <b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>3</sup><br>According to International Patent Classification (IPC) or to both National Classification and IPC<br>INT. CL. C01B 33/02<br>US. CL. 423-350  |   |                                     |   |   |  |  |   |     |   |   |     |   |  |     |   |   |        |   |   |        |   |   |     |
|---|---|-------------------------------------|---|---|--|--|---|-----|---|---|-----|---|--|-----|---|---|--------|---|---|--------|---|---|-----|
| <b>II. FIELDS SEARCHED</b><br><div style="text-align: right; margin-right: 100px;">Minimum Documentation Searched <sup>4</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; text-align: left; border-bottom: 1px solid black;">Classification System</th> <th style="text-align: left; border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">US</td> <td style="border: 1px solid black; padding: 5px;">423-349, 350, 341, 490</td> </tr> </table> <div style="text-align: center; margin-top: 5px; font-size: small;">           Documentation Searched other than Minimum Documentation<br/>           to the Extent that such Documents are Included in the Fields Searched <sup>5</sup> </div>  |   |                                     | Classification System   | Classification Symbols  | US   | 423-349, 350, 341, 490   |   |     |   |   |     |   |  |     |   |   |        |   |   |        |   |   |     |
| Classification System   | Classification Symbols  |                                     |   |   |  |  |   |     |   |   |     |   |  |     |   |   |        |   |   |        |   |   |     |
| US  | 423-349, 350, 341, 490  |                                     |   |   |  |  |   |     |   |   |     |   |  |     |   |   |        |   |   |        |   |   |     |
| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; text-align: left; border-bottom: 1px solid black;">Category <sup>6</sup></th> <th style="text-align: left; border-bottom: 1px solid black;">Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup></th> <th style="width: 15%; text-align: left; border-bottom: 1px solid black;">Relevant to Claim No. <sup>18</sup></th> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="border: 1px solid black; padding: 5px;">N, J. Electrochem. Soc., 128:1<br/>January 1981, A. Sanjurjo et al.<br/>pages 179-184</td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">1-8</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="border: 1px solid black; padding: 5px;">US, A, 2,941,867 (Maurer)<br/>21 June 1960</td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">1-8</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="border: 1px solid black; padding: 5px;">US, A, 4,169,129 (Keeton)<br/>25 September 1979</td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">3-8</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="border: 1px solid black; padding: 5px;">US, A, 4,298,586 (Sidkar)<br/>03 November 1981</td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">1, 4-8</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="border: 1px solid black; padding: 5px;">US, A, 3,793,436 (Hartig)<br/>19 February 1974</td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">1, 4-8</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="border: 1px solid black; padding: 5px;">US, A, 3,963,838 (Setty et al.)<br/>15 June 1976</td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">1-8</td> </tr> </table> |   |                                     | Category <sup>6</sup>   | Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>  | Relevant to Claim No. <sup>18</sup>                          | X  | N, J. Electrochem. Soc., 128:1<br>January 1981, A. Sanjurjo et al.<br>pages 179-184 | 1-8 | Y | US, A, 2,941,867 (Maurer)<br>21 June 1960 | 1-8 | Y | US, A, 4,169,129 (Keeton)<br>25 September 1979 | 3-8 | Y | US, A, 4,298,586 (Sidkar)<br>03 November 1981 | 1, 4-8 | A | US, A, 3,793,436 (Hartig)<br>19 February 1974 | 1, 4-8 | A | US, A, 3,963,838 (Setty et al.)<br>15 June 1976 | 1-8 |
| Category <sup>6</sup>   | Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>  | Relevant to Claim No. <sup>18</sup> |   |   |  |  |   |     |   |   |     |   |  |     |   |   |        |   |   |        |   |   |     |
| X   | N, J. Electrochem. Soc., 128:1<br>January 1981, A. Sanjurjo et al.<br>pages 179-184   | 1-8                                 |   |   |  |  |   |     |   |   |     |   |  |     |   |   |        |   |   |        |   |   |     |
| Y   | US, A, 2,941,867 (Maurer)<br>21 June 1960   | 1-8                                 |   |   |  |  |   |     |   |   |     |   |  |     |   |   |        |   |   |        |   |   |     |
| Y   | US, A, 4,169,129 (Keeton)<br>25 September 1979  | 3-8                                 |   |   |  |  |   |     |   |   |     |   |  |     |   |   |        |   |   |        |   |   |     |
| Y   | US, A, 4,298,586 (Sidkar)<br>03 November 1981   | 1, 4-8                              |   |   |  |  |   |     |   |   |     |   |  |     |   |   |        |   |   |        |   |   |     |
| A   | US, A, 3,793,436 (Hartig)<br>19 February 1974   | 1, 4-8                              |   |   |  |  |   |     |   |   |     |   |  |     |   |   |        |   |   |        |   |   |     |
| A   | US, A, 3,963,838 (Setty et al.)<br>15 June 1976   | 1-8                                 |   |   |  |  |   |     |   |   |     |   |  |     |   |   |        |   |   |        |   |   |     |
| <div style="display: flex; justify-content: space-between;"> <div style="width: 50%;"> <p><sup>15</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p> </div> </div>   |   |                                     |   |   |  |  |   |     |   |   |     |   |  |     |   |   |        |   |   |        |   |   |     |
| <b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">           Date of the Actual Completion of the International Search <sup>1</sup><br/><br/>           11 March 1983         </td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">           Date of Mailing of this International Search Report <sup>2</sup><br/> <div style="text-align: center; font-size: large; font-weight: bold;">12 APR 1983</div> </td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;">           International Searching Authority <sup>1</sup><br/><br/>           ISA/US         </td> <td style="border-bottom: 1px solid black; padding: 5px;">           Signature of Authorized Officer <sup>20</sup><br/> <div style="text-align: center;">              Oscar R. Vertiz           </div> </td> </tr> </table>   |   |                                     | Date of the Actual Completion of the International Search <sup>1</sup><br><br>11 March 1983 | Date of Mailing of this International Search Report <sup>2</sup><br><div style="text-align: center; font-size: large; font-weight: bold;">12 APR 1983</div> | International Searching Authority <sup>1</sup><br><br>ISA/US | Signature of Authorized Officer <sup>20</sup><br><div style="text-align: center;">              Oscar R. Vertiz           </div> |   |     |   |   |     |   |  |     |   |   |        |   |   |        |   |   |     |
| Date of the Actual Completion of the International Search <sup>1</sup><br><br>11 March 1983   | Date of Mailing of this International Search Report <sup>2</sup><br><div style="text-align: center; font-size: large; font-weight: bold;">12 APR 1983</div> |                                     |   |   |  |  |   |     |   |   |     |   |  |     |   |   |        |   |   |        |   |   |     |
| International Searching Authority <sup>1</sup><br><br>ISA/US  | Signature of Authorized Officer <sup>20</sup><br><div style="text-align: center;">              Oscar R. Vertiz           </div>                            |                                     |   |   |  |  |   |     |   |   |     |   |  |     |   |   |        |   |   |        |   |   |     |

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

|   |  |     |
|---|--|-----|
| A | US, A, 2,999,736 (Shalit)<br>12 September 1961       | 1-8 |
| A | US, A, 4,188,368 (Wolf et al)<br>12 February 1980    | 1-8 |
| A | US, A, 2,172,969 (Eringer)<br>12 September 1939      | 1-8 |
| A | US, A, 3,041,145 (Ariesl)<br>26 June 1962            | 1-8 |
| A | DE, B, 1,122,501 (Andrieux et al)<br>25 January 1962 | 1-8 |

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE <sup>10</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers \_\_\_\_\_, because they relate to subject matter <sup>12</sup> not required to be searched by this Authority, namely:

2. ☐ Claim numbers \_\_\_\_\_, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out <sup>13</sup>, specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING <sup>11</sup>

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

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